Humic Acids Form Brown Coal Mechanically Treated in the Presence of Air

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Abstract

Efficiency of brown coal oxidation under various conditions including those of mechanical activation is investigated. It is established that mechanical treatment accelerates coal oxidation thus increasing the yield of humic acids. As shown in the NMR ^{13}C investigation, humic acids from the initial and mechanically treated coal samples substantially differ in the structural-group composition. Field tests showed that humic acids from mechanically treated coal samples possess higher physiological activity, which affects an increase in crop capacity of agricultural plants.

INTRODUCTION

One of the factors determining soil fertility is high humus content. Physiologically active substances incorporated in humus stimulate plant development. A similar effect is caused also by the main components of humus – humic acids (HA) extracted from natural organic raw material. Enormous experimental data accumulated by present provide evidence of the positive effect of coal humic fertilizers on crop capacity and quality of agricultural plants [1–4].

Humic acids are natural high-molecular systems of non-regular structure; they are widespread in nature (turf, brown and oxidized coal, soil, bottom sediments, *etc.*) and play a very important part in providing vital activity of ecosystems. Humic acids are used in accumulator industry and as surfactants. However, they are most widely used in agriculture as fertilizers. In addition to acceleration of plant growth, HA perform also some other functions, in particular resistance (they elevate disease resistance), transport (good complexing agents and transporters of metal ions), *etc.* [1, 2]. Especially important role of HA is weakening of unfavourable external factors, elimination of the negative action of high doses of mineral fertilizers and the hazardous effect of soil fatiguing substances, removal of plant toxicosis [3, 4].

Large resources of brown and oxidized coal in East Siberia serve as the main source for obtaining HA and comprise the necessary basis for their production [5, 6]. The main obstacle to large-scale use of HA is the absence of technologies allowing one to carry out almost complete transfer of the organic mass of coal into HA, and the problem of the use of mineral constituents of coal. In addition, the problem of obtaining HA with required physiological activity (PA).

It is necessary to state that the opinions on the nature of PA of HA are contradictory up to now; the question about structural features and characteristics of HA molecules that determine the level of their PA requires further investigation involving new up-to-date methods. One of these methods is quantitative nuclear magnetic resonance (NMR) spectroscopy, which opens wide possibilities for identification and quantitative determination of the structuralgroup composition of HA [7–9].

An increase in the yield of HA from the organic substance of brown coal can be achieved either by carrying out oxidation processes or by dispersing and mechanochemical activation of the initial material [10, 11].

Different kinds of coal interact with oxygen of the air to a definite extent depending on the structure and properties of organic compounds incorporated in them [12, 13]. Coal oxidation under natural conditions is unfavourable process in the major part of cases because it causes worsening of energygenerating and technological characteristics of coal as a fuel, and their chemical properties important for their further processing as a raw material. An exception is the directed oxidation of coal with different reagents aimed at the investigation of the structure of compounds included into the organic matter of carbon (OMC) and in some cases extraction of target chemical products formed during oxidation [13]. Oxidation of coal by different reagents under relatively mild conditions leads to partial chemical destruction of the high-molecular components of the organic matter and to a substantial increase in the amount of oxygen-containing functional groups [12–14]. The presence of the latter, first of all carboxylic and phenoxyl groups, allows one to determine the solubility of OMC in alkaline solutions; therefore, HA content can be determined.

It was established [14, 15] that the mechanism of coal oxidation processes can be described taking into account the main ideas of the theory of radical chain reactions. It was shown on the basis of experimental results [12] that, with other conditions being identical, one of the factors determining the rate of OMC interaction with oxygen of the air is the specific surface of coal.

Milled coal is used in technological processes. However, in the majority of cases, dispersion of coal in the presence of air and its possible interaction with oxygen are not taken into account. It should also be noted that, along with a decrease in particle size and increase in specific surface under intense mechanical action on coal in dispersing devices providing impacts of rather high energy, effective mechanochemical activation of OMC takes place. This is especially well noticeable in the case when the size of coal particles reach several tens micrometers. This is accompanied by partial mechanical destruction of relatively high-molecular OMC components, which causes substantial changes in the physicochemical properties of coal [10, 11], an increase in coal reactivity toward different reagents, an increase in coal solubility in various solvents. Mechanical activation and mechanical destruction of OMC, similarly to oxidation, proceed through the stage of free radical formation [16, 17]. It is evident that combination of mechanochemical activation and oxidation should substantially promote an increase in the yield of HA and intensify this process.

The goal of the present work was to investigate the effect of mechanical activation of coal under different conditions on the efficiency of its oxidation by oxygen of the air, yield and qualitative composition of HA, and to estimate the efficiency of HA as plant growth stimulators.

EXPERIMENTAL

The subject of investigation was the analytical samples of brown coal from East Siberia (Khanda, Shchetkinskoye, Glinkinskoye deposits of the Irkutsk Basin, Berezovka and Irsha-Borodino deposits of the Kansk-Achinsk Basin) with particle size ≤250 μm. The results of technical analysis and elemental composition are shown in Table 1. Humic acids from the initial and mechanically treated coal were extracted using a standard procedure by treating with 1 % NaOH solution.

Oxidation of the initial coal under stationary conditions was carried out in sealed vessels placed in a thermostat at different temperature (60, 75, 100, 110, and 120 °C). Oxidation time was up to 100 h. Gases were sampled and analyzed after definite time intervals.

The mechanochemical treatment of coal was carried out in grinding activator AI-2 (a planetary-type mill, theoretically calculated velocity of milling balls: 18 m/s), in a laboratory-rocking mill LMK (theoretically

TABLE 1

Results of technical analysis and the elemental composition of the initial coal samples

Coal from deposits	Designation	W^a	A^d	S_t^d	Elemental composition, % daf				
					C	H	N	S	O
Glinkinskoye	GI	4.7	9.90	0.45	68.17	4.78	1.22	0.20	25.62
Shchetkinskoye	ShchI	18.8	8.19	0.78	60.58	6.24	1.52	0.62	31.04
Khanda	KhI	3.4	25.20	0.77	68.34	6.10	0.59	0.67	24.30
Berezovka	BKA	3.9	6.77	0.86	71.33	5.25	0.54	0.73	22.15
Irsha-Borodino	IBKA	4.3	11.41	0.34	71.26	4.97	0.96	0.25	22.56

calculated velocity of milling balls: 2 m/s), in a multi-purpose disintegrator UDA (a flow-through type apparatus, the linear velocity of rotating discs: 150 m/s). Treatment in AI-2 and in LMK was carried out under the optimal conditions (treatment time: 15 and 120 min, respectively [18]) in sealed vessels, followed by sampling and analysis of the qualitative and quantitative composition of the gaseous products. The air to OMC ratio was constant in all the experiments and equal to 10 ml/g, the oxygen to OMC ratio was 2.1 ml/g.

The disperse state of the initial and mechanically treated coal samples was determined with a scanning photosedimento-gtaph Analysette-20 (Fritsch company). The main parameter for comparing the degree of grinding was the median diameter d_m – the size of particles (in mm) the content of which in the sample, together with the particles of smaller size, accounts for 50 % (mass).

The quantitative and qualitative composition of gases was determined with Tsvet-530 chromatograph. Helium was used as a carrier gas. Relative amounts of gases were calculated on the basis of peak areas. The absolute amounts of reacted oxygen were determined on the basis of constancy of the absolute amount of nitrogen present in the air (the admission of a constant absolute amount of oxygen in a sealed vessel is quite reasonable). Coal oxidation under stationary conditions and during mechanochemical treatment was considered at the first approximation as a first-order reaction with respect to oxygen. Rate constants were calculated on the basis of changes in oxygen concentration with time [12].

RESULTS AND DISCUSSION

The results of determination of the amount of reacted oxygen listed in Table 2 and the calculated rate constants of oxidation of the Khanda coal during its oxidation under different conditions show that the rate of coal oxidation under stationary conditions is determined only by temperature. An increase in temperature by 10 °C results in an increase in the rate constant by a factor of approximately 1.15. The rate constant increases substantially during mechanical treatment of coal in the presence of air. For mechanical treatment of coal in LMK, where a low-energy impact is realized, activation of OMC practically does not occur. An increase in the rate constant by a factor of about 10 in comparison with the value for the conditions of stationary oxidation at 60 °C is due exclusively to an increase in specific area of coal as a result of its dispersion. The d_m values are 90 and 30 μm for the initial coal sample and that treated in LMK. Evidently, this is the main factor affecting an increase in the yield of HA. It should be stressed that the rate constants of oxidation and HA yield from coal oxidized at 125 °C for 240 min under stationary conditions and from coal treated mechanically with LMK for 120 min at room temperature are approximately the same. Therefore, we may conclude that coal dispersing in LMK affects the rate of oxidation and yield of HA in the same manner as an increase in temperature by about 100 °C does.

Though changes in the specific surface of coal under oxidation affects its reactivity in the reactions involving its interaction with the oxygen of air, the effect of mechanical acti-vation during coal oxidation under mechanical

TABLE 2

Characteristics of the oxidation of coal from the Khanda deposit

Oxidation conditions		Amount of reacted oxygen, ml/g	Oxidation rate constant $K \cdot 10^2$, ml/g · min	HA yield, % daf
Time, min	T, °C			
240[a]	60	0.15	0.44	32.6
240[a]	75	0.58	1.92	35.6
240[a]	100	0.97	3.22	37.2
240[a]	110	1.62	3.79	37.8
240[a]	125	1.89	4.35	41.3
120[b]	Room	0.61	3.95	42.5
15[c]	60[e]	1.43	88.8	54.9
15[d]	60[e]	0.0	0.0	39.8

[a]Time of oxidation under stationary conditions.
[b]Time of mechanical treatment with LMK in the presence of air.
[c]Time of mechanical treatment with AI-2 in the presence of air.
[d]Temperature of maximal heating of the cylinders during mechanical treatment.
[e]Time of mechanical treatment with AI-2 in nitrogen.

treatment is more substantial. The contribution of the latter also determines the yield of HA to a larger extent. After mechanical treatment of coal in AI-2 for 15 min, d_m is 30 μm, that is, it coincides with the value for coal treated in LMK for 2 h. However, the rate constant of the interaction of the oxygen of air increases in this case by a factor of 20, and the yield of HA by 25 %. It is evident that in this case, along with an increase in the specific surface, the main factor is mechanical activation of coal. On the one hand, mechanical destruction of the high-molecular components of OMC occurs; on the other hand, active centres are formed, and they interact efficiently with the oxygen of air; this explains the observed changes in the rate constant and in HA yield. In this situation, it is more reasonable to speak of the oxidative mechanical destruction proceeding under high-energy mechanical action in the presence of oxygen. This is also confirmed by the fact that mechanical treatment of coal in AI-2 for 15 min in nitrogen causes an increase in the yield of HA by only 7 %.

The yield of HA from the initial coal and that treated in different mechanochemical devices is shown in Table 3. The yield of HA in all the experiments was much higher from mechanically treated samples than from the initial ones. Mechanical treatment in AI-2 leads to a much larger increase in HA yield (by 18–40 %) than treatment in UDA does (by 5–25 %). It is evident that in this case the determining factors are the duration of mechanical treatment and time of contact of coal under activation with oxygen of air. The UDA disintegrator is a flow type apparatus; time of contact with oxygen is several tenths of a second. So, the UDA apparatus is preferable from the technological point of view, though the yield of HA is somewhat lower in the latter case.

It follows from the data shown in Table 3 that the yield of HA from mechanically treated coal depends on the nature of initial coal. The latter parameter determines the efficiency of its mechanical destruction and interaction with oxygen. The qualitative composition of HA from mechanically treated coal differs from that of HA from the initial coal. Results of ^{13}C NMR determination of structural-group composition of HA obtained from the initial and mechanically treated coal are listed in Table 4.

A detailed analysis of these data allows us to state that mechanical treatment, and finally oxidative mechanical destruction of coal, along with an increase in the yield of HA cause substantial changes in their structural-group composition. Some common trends can be noted. The content of aromatic structures is lower in HA from mechanically treated coal than that in HA from initial coal samples (except GI coal); the number of methoxy groups and carbohyd-

TABLE 3

Yield of humic acids HA from the initial and mechanically treated coal, % daf

Coal number	Coal initial	mechanically activated	
		AI-2*	UDA
GI	66.9	90.1	80.2
ShchI	33.5	73.9	54.3
KhI	33.5	54.9	47.2
BKA	11.2	47.8	35.4
IBKA	18.3	36.7	22.8

*Mechanical treatment for 15 min.

rate fragments (C_{alk}–O) decreases, which is likely to be due to the set of processes of their efficient oxidation and mechanical destruction; the HA from mechanically treated coal contain increased total amount of oxygenated functional groups $\sum$(C–O) due to an increase in the amount of carbonyl, carboxyl and phenoxyl fragments, which is a consequence of efficient oxidation of OMC.

These results show that oxidative mechanical destruction of OMC proceeds during mechanical treatment of coal, which promotes an increase in HA yield and causes changes in their qualitative (structural-group) composition.

One of the main resulting effects of mechanical activation of coal is mechanical destruction of the high-molecular components of coal, which increases the yield of HA from mechanically activated coal. In addition, mechanical activation of coal in the presence of oxygen of the air increases the rate of coal oxidation, which is another factor increasing the yield of HA. The entire set of oxidation and mechanical activation processes intensify destruction of OMC to a substantial extent. In this case, it is reasonable to speak of oxidative mechanical destruction of coal.

One of the main features of HA extracted from mechanically activated coal is that their group and structural composition is substantially different from that of HA from initial coal. Correspondingly, their PA, in particular their effect on germination, growth and productivity of plants can be substantially different. A detailed investigation of the quantitative and qualitative composition of HA extracted using different procedures will allow us to increase the yield of HA, on the one hand, and to obtain HA with the required PA, on the other hand.

CONCLUSIONS

The following conclusions can be made on the basis of results obtained in the investigation aimed at extraction of HA from a large set of coal samples from East Siberia (coal from

TABLE 4

Content of carbon atoms in different structural fragments of HA extracted from initial and mechanically activated coal, according to the data of ^{13}C NMR spectra, rel. %

Structural fragment	Content in coal* GI	ShchI	KhI	BKA	IBKA
C_{alk}	18.31/6.5	22.9/17.9	34.0/30.4	28.2/30.4	25.3/23.1
C_{alk}–O	2.6/0.9	4.0/3.8	9.2/7.4	4.4/2.6	6.2/4.8
C_{ar}	48.7/50.6	48.9/46.3	36.4/31.6	50.9/39.9	47.4/45.0
C_{ar}–O	9.1/10.4	10.6/11.4	7.3/10.1	7.7/11.0	8.6/10.1
–COO–	15.5/16.4	12.2/16.4	11.4/14.5	8.5/12.5	10.1/12.1
C=O	5.6/6.2	1.4/4.2	1.9/5.9	0.3/3.6	2.4/4.9
$\sum$(C–O)	32.8/33.9	28.2/35.8	29.2/37.9	20.9/29.7	27.3/31.9
f_a**	0.58/0.61	0.60/0.58	0.44/0.42	0.59/0.51	0.56/0.55

Notes. 1. In all the cases, mechanical treatment was carried out in AI-2 for 15 min in the presence of air. 2. The data [7] on the content of: carbon atoms in alkyl groups (C_{alk}); carbon atoms of alkyl groups at the oxygen atom, including those of carbohydrate fragments (C_{alk}–O); carbon atoms in aromatic structures (C_{ar}); carbon atoms in aromatic structures at the α oxygen atom (C_{ar}–O); carbonyl carbon atoms (C=O); the sum of carbon atoms at the oxygen atom ($\sum$(C–O)).

* The first value is the content in the initial coal, the second one – in mechanically treated ones.

**f_a is degree of aromaticity.

TABLE 5

Effect of humic acids (HA) on the crop capacity of agricultural plants [19]

HA	Crop capacity*		
	Wheat	Barley	Pea
Extracted from the initial KhI	25.1/120.6	67.7/157.5	48.6/153.8
The same, mechanically treated in AI-2	31.0/149.2	76.4/177.8	27.5/87.1
The same, from the initial BKA	29.6/142.1	70.1/163.1	38.5/121.8
The same, mechanically treated in AI-2	32.3/155.3	49.9/116.0	12.3/38.8
Reference	20.8/100.0	43.0/100.0	31.6/100.0

*The first value is in centners per hectare, the second one is in percent.

Berezovka and Irsha-Borodino deposits of the Kansk-Achinsk Basin; from Khanda, Shchetkinskoye, Glinkinskoye deposits of the Irkutsk Basin) using different procedures:

1. Mechanical treatment in machines providing low-energy mechanical action (ball mills) in the presence of air, though allowing one to obtain coal particles 60–100 μm in size, has only insignificant effect on the yield of HA increasing it only by not more than 10 %.

2. Mechanical activation of brown coal in an inert atmosphere (nitrogen) causes an increase in the yield of HA by 15–25 % due to the set of processes involving coal grinding, increase in its specific surface, opening of micro- and macropores that were previously inaccessible for an alkali, washing native HA out of these pores, mechanical destruction and a decrease in the mean molecular mass of the main components of the organic mass of coal. A method of mechanical action and the efficiency of mechanical activation are determining for an increase in the yield of HA.

3. Mechanochemical activation of coal in the presence of oxygen of the air promotes an increase in the yield of HA and their simultaneous enrichment with oxygen-containing functional groups, accompanied with a decrease in the relative content of aromatic structural fragments.

Investigation of the effect of HA on the productivity of agricultural plants was carried out with HA obtained from the initial brown coal and mechanically treated one from two deposits (see Table 5) [19]. The consumption of HA was 200 g/ha, calculated for the dry substance (alkaline solutions of HA with the concentration of 0.016 % were used).

In addition, the following aspects should be mentioned:

1. Humic acids, both those form the initial coal and from mechanically activated one, cause an increase in the productivity of grain crops (wheat, barley, corn). The efficiency of the former HA does not exceed 15 %, while HA from coal subjected to preliminary oxidative mechanical destruction causes an increase in the productivity by 25–35 %.

2. The productivity of legumes (pea) increases by 15–20 % after HA from initial coal are introduced, while HA from mechanically activated coal cause a substantial negative effect decreasing the productivity by 20–25 %.

On the basis of the results obtained, one may speak of the promising character of the methods of oxidative mechanical destruction of coal, both with respect to an increase in the yield of HA from coal and for the purpose of obtaining HA with increased PA to agricultural plants.

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